

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

# PATENT SPECIFICATION

(11) 1 514 224

1 514 224

- (21) Application No. 25323/75 (22) Filed 13 June 1975  
 (31) Convention Application No. 485399  
 (32) Filed 3 July 1974 in  
 (33) United States of America (US)  
 (44) Complete Specification published 14 June 1978  
 (51) INT CL<sup>2</sup> B32B 5/20 27/12 31/20//27/30  
 (52) Index at acceptance  
 B5N 0520 0524 0532 2712 2730 3120 3300



B2E 178 180 182 184 186 18Y 204 20Y 217 219 21Y 236 237 239  
 23Y 246 247 253 25Y 268 269 289 299 308 323 327 335  
 336 337 339 345 34Y 352 353 354 355 356 357 359 35Y  
 36Y 390 391 392 39Y 435 436 43Y 441 446 447 44Y 452  
 453 456 457 463 464 467 46Y 473 475 477 478 485 486  
 487 48Y 497 498 49Y 510 515 516 517 519 51X 523 527  
 52Y 532 533 536 537 545 546 547 549 54Y 555 556 557  
 559 55Y 562 563 564 565 566 567 568 569 56Y 572 576  
 577 579 57Y 58Y

## (54) SIMULATED LEATHER

(71) We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with composites made of a plurality of crushed foam/fabric layers, the composite having a surface finish film. The film may for example be a transparent preformed film, which film can be suitably coated or printed with a design, or it may be a film formed *in situ* for example from a coating of melamine resin, urea formaldehyde condensate, nitrocellulose, polyurethane, poly vinyl chloride, acrylic, cellulose acetate butyrate, nitrocellulose modified polyurethane or a mixture thereof. The composites may simulate leather and may be used in virtually all areas where real leather can be used, for example, in upholstery, apparel, handbags, luggage and footwear.

There are three essential components in the laminate. The first is fabric, the second is crushed foam (as hereinafter defined) and the third is the surface finish on a laminate of a multiplicity of layers of the crushed-foam coated fabric. By varying the composition of these three components, it is possible to prepare products which will vary in hand, resilience and stretch.

By a crushed foam in this specification and Claims we mean a foam which has been compressed to reduce its thickness and leave cells separated by thin interconnected walls.

Any of the numerous fabrics known for use in the manufacture of leather substitutes can be employed in this invention and the choice of fabrics is largely dependent upon the intended end use of the product. Typical textile fabrics are: cotton, twill, broadcloth, acetate or polyester crepe, rayon challis, polyester knit, double knit and nylon taffeta and tricot. In addition to these materials, there can also be employed fiberglass, "Spandex" (Registered Trade Mark) knits, woollens and worsteds, flocked fabrics, rayon fabrics and blends of natural and synthetic fibres. In addition to fabrics, imitation leathers can be used and references to fabrics hereinafter should also be regarded as referring to these materials. The textile may be simply a functional supporting substrate or a textile having a pre-finished "face" to serve as the outer surface of the composite or as a lining. An example is a synthetic pile fur fabric, the back of which may function as the supporting substrate for the composite so that the final composite has two functional and aesthetically appealing surfaces. Such a composite could be used to make a reversible garment which would have a leather-like texture on one side and a fur texture on the other. Naturally, the nature of the particular fabric employed will have a pronounced effect on the hand of the laminate. For example, acetate crepe may be used to give a laminate with a bouncy resilient hand. A cotton twill, on the other hand, may be used to give a laminate with a less bouncy hand but more drape. In addition to yielding products having different hand and resiliency characteristics, this invention also permits the control of resiliency and hand by varying the fabric orientation between one crushed foam coated fabric

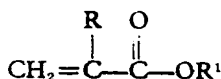
Takes care of claims 1 and 3-4

layer and another. It is well-known that most woven fabrics have a higher degree of stretch in the fill direction than in the warp direction. Thus, in the articles of this invention if the two fabric layers are orientated in the same direction, the laminate will have more stretch in one direction than the other. If the fabrics are orientated at varying angles, then the final crushed foam coated fabric laminate may be given a more uniform stretch in different directions.

The compositions employed to produce the foam may be latices of polymers of at least two of the following monomers of which at least one is a monomer which contains functional groups capable of crosslinking:

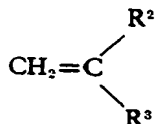
(a)  $\alpha, \beta$  - ethylenically unsaturated acid such as acrylic acid, methacrylic acid, ethacrylic acid, itaconic acid, aconitic acid, crotonic acid, citraconic acid, maleic acid, fumaric acid,  $\alpha$ -chloroacrylic acid, cinnamic acid and mesaconic acid;

(b) monomer of the formula

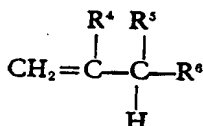


wherein R is hydrogen or alkyl, for example,  $\text{C}_1$  to  $\text{C}_4$  alkyl, and  $\text{R}^1$  is a straight, branched or cyclic alkyl, alkoxyalkyl or alkylthioalkyl radical having from 1 to 20 carbon atoms, such as methyl, ethyl, propyl, *n*-butyl, 2-ethylhexyl, heptyl, hexyl, octyl, 2-methylbutyl, 1-methylbutyl, butoxybutyl, 2-methylpentyl, methoxymethyl, ethoxyethyl, cyclopentyl, cyclohexyl, isobutyl, ethylthioethyl, methylthioethyl, ethylthiopropyl, 6-methylnonyl, decyl, dodecyl, tetradecyl or pentadecyl;  $\text{R}^1$  may also be ureido, hydroxyalkyl of from 1 to 5 carbon atoms, i.e. hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxybutyl or hydroxypentyl, 2,3 - epoxypropyl, amino ( $\text{C}_1$  to  $\text{C}_5$ )-alkyl, mono- or di- ( $\text{C}_1$  to  $\text{C}_5$ )-alkyl or hydroxy ( $\text{C}_1$  to  $\text{C}_5$ )-alkyl substituted amino ( $\text{C}_1$  to  $\text{C}_5$ )-alkyl;

(c) monomer of the formula



wherein  $\text{R}^2$  is hydrogen or methyl and  $\text{R}^3$  is halo such as chloro, ( $\text{C}_1$  to  $\text{C}_5$ )-alkanoyloxy such as acetoxy, cyano, formyl, phenyl, carbamoyl, N - hydroxymethyl carbamoyl, tolyl, methoxymethyl, 2,4 - diamino - s - triazinyl - ( $\text{C}_1$  to  $\text{C}_5$ ) - alkyl, or epoxy; and (d)

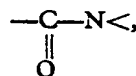


wherein  $\text{R}^4$  is hydrogen or methyl;  $\text{R}^5$  and  $\text{R}^6$  are ( $\text{C}_1$  to  $\text{C}_5$ )-alkoxy such as methoxy and ethoxy, or ( $\text{C}_1$  to  $\text{C}_5$ )-alkanoyloxy such as acetoxy.

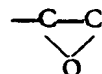
Examples of the specific monomers (b), (c) and (d) which may be employed are:

methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, *n*-butyl methacrylate, isobutyl methacrylate, *sec*-butyl methacrylate, *tert*-butyl methacrylate, pentyl methacrylate, isopentyl methacrylate, *tert*-pentyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, 2-ethylbutyl methacrylate, 2 - ethylhexylmethacrylate, octyl methacrylate, decyl methacrylate, lauryl methacrylate, myristyl methacrylate, cetyl methacrylate, stearyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, *sec*-butyl acrylate, *tert*-butyl acrylate, amyl acrylate, isoamyl acrylate, *tert*-amyl acrylate, hexyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, vinyl acetate, tetradecyl acrylate, acrylamide, pentadecyl acrylate, styrene, pentadecyl methacrylate, vinyl toluene, methacrylamide, N-methylolacrylamide, glycidyl methacrylate, methylaminoethyl methacrylate, *tert*-butylaminoethyl methacrylate, 6 - (3 - butenyl)-2,4 - diamino - s - triazine, hydroxypropyl methacrylate, hydroxyethyl methacrylate, methacrylonitrile, methoxymethyl methacrylamide, N - methylol methacrylamide, acrolein, methacrolein, 3,4 - epoxy - 1 - butene, acrolein diethyl acetal, acrolein dimethyl acetal, allylidene diacetate, methallylidene diacetate.

The crosslinkable addition polymerizable unsaturated monomers may have reactive polar groups selected from  $-\text{OH}$ ,  $-\text{SH}$ ,  $>\text{NH}$ ,



$-\text{N}=\text{C}=\text{O}$ ,  $>\text{CHCN}$ ,  $-\text{CHO}$ ,  $-\text{COOH}$  and



Such groups may be included as are mutually or self-crosslinkable, or separate crosslinking compounds such as triazineformaldehyde resin may be added.

Of course, water-sensitive materials such as isocyanates should not be used in aqueous systems unless they are blocked by reaction with a phenol group which protects the isocyanate groups until subsequent heating or the use of other reaction mechanisms such as the use of calcium, zinc, or tin compound catalyst conventional in the art.

The preferred copolymers have a molecular

weight of from 70,000 and 2,000,000 and preferably 250,000 to 1,000,000 and are made by emulsion copolymerization of the several monomers in the proper proportions. Conventional emulsion polymerization techniques are described in U.S. Pat. Nos. 2,754,280 and 2,795,654. Thus, the monomers may be emulsified with an anionic, a cationic, or a nonionic dispersing agent, 0.05 to 10 percent thereof ordinarily being used on the weight of the total monomers. The acid monomer and many of the other functional or polar monomers may be soluble in water so that the dispersing agent serves to emulsify the other monomer or monomers. A polymerization initiator of the free radical type, such as ammonium or potassium persulfate, may be used alone or in conjunction with an accelerator, such as potassium metabisulfite or sodium thiosulfate. Organic peroxides, such as benzoyl peroxide and *tert*-butyl hydroperoxide are also useful initiators. The initiator and accelerator, commonly referred to as catalyst, may be used in proportions of 0.1 percent to 10 percent each based on the weight of monomers to be copolymerized. The amount, as indicated above, may be adjusted to control the intrinsic viscosity of the polymer. The temperature may be from room temperature to about 260°C.

The following is a list of some of the copolymers which may be employed in this invention. The copolymers have the following monomer compositions:

- 35 96EA/3.5AM/0.5AA; 96EA/4MOA;  
 94EA/5.5ALACAC/0.5AA;  
 94.5EA/5HEMA/0.5AA;  
 66EA/32.7MMA/1.3MAA;  
 83EA/15MMA/2AA;  
 40 83BA/15AN/1AC/1AA;  
 65EA/25.5BA/4.5AN/3.5AM/1.5IA;  
 86EA/10AN/4MOA;  
 83BA/14AN/1Ac/2AA;  
 96EA/1Ac/2AA;  
 45 68BA/28MMA/2Ac/2AN;  
 30BA/55EA/10MMA/3.5AN/0.5Ac/1AA  
 and  
 45BA/10AN/40EA/4HEMA/1AA.

The definitions of the abbreviations are:  
 50 EA=ethyl acrylate; BA=butyl acrylate;

MMA=methyl methacrylate; AA=acrylic acid; MAA=methacrylic acid; IA=itaconic acid; HEMA=hydroxy ethyl methacrylate; AN=acrylonitrile; Ac=acrolein;

ALACAC=allyl acetoacetate;

MOA=acrylamide N - methylol acrylamide (1:1) and AM=acrylamide.

The use of a water soluble surfactant or a combination of surfactants increases the dispersion of the latex emulsion and acts as a foaming aid and foam stabilizer.

These surfactants include the alkali metal, ammonium or amine salts such as the mono-, di- or triethanol amines of the aliphatic carboxylic acids having from 16 to 20 carbon atoms including oleic acid and stearic acid; for example, sodium, potassium or ammonium stearate; sodium, potassium and ammonium oleate. Other surfactants which may be employed together with those described above include the alkali metal salts of aliphatic or alkylaryl sulfonic acids, such as sodium lauryl sulfate and sodium dodecylbenzene sulfonate as well as nonionic surfactants such as the polyethylene oxide condensates of the alkyl phenols or higher fatty alcohols, for example, *tert*-octylphenol condensed with from 5 to 40 ethylene oxide units, lauryl alcohol condensed with from 5 to 50 ethylene oxide units or similarly ethylene oxide condensates of long chain mercaptans, fatty acids and amines.

Although either thermoset or thermoplastic resins may be employed, the preferred resins are the thermoset ones since the foam generated affords products more desirable in the manufacture of and subsequent use of simulated leather.

To crosslink the acrolein or methacrolein containing resins, a dibasic amine, for example, diethylene triamine, and hydrazine are employed. The melamine type resins are used to crosslink the polymers containing hydroxy and amino functions. Other crosslinking agents may be employed and said agents are well-known to those skilled in the art.

The latex, when formulated with the foam stabilizer and optionally, suitable pigments, is readily convertible into foamed state. The polymer composition is preferably such that excessive thickening of the formulation is not encountered under the acid or alkaline conditions employed to assure the most efficient operation of the foam stabilizing agent. In addition, the copolymer is preferably such that the crushed foam retains its softness and its flexibility at low temperatures, for example, to a temperature as low as -20°C, and after curing is non-tacky. In addition, the foam is resistant to washing in normal detergents used for cleaning of textiles in general and drapery fabrics in particular and is resistant to dry-cleaning. By providing a foam that is durable to dry-cleaning and to washing

the foam is quite useful for textiles which are frequently subjected to drycleaning and washing operations.

An important property of the polymer for both the foam and the clear film is the glass transition temperature ( $T_g$ ) thereof, and consequently the selection of monomers and proportions thereof depends upon their influence on the  $T_g$ . The  $T_g$  of the polymer for the foam is suitably between  $-60^\circ\text{C}$  and  $35^\circ\text{C}$ . For the clear film, it is normally between  $-30^\circ\text{C}$  and  $100^\circ\text{C}$ . " $T_g$ " is a conventional criterion of polymer hardness and is described by Flory, "Principles of Polymer Chemistry", pp. 56 and 57 (1953), Cornell University Press. While actual measurement of the  $T_g$  is preferred, it may be calculated as described by Fox, Bull. Am. Physics Soc. 1, 3 p. 123 (1956). Examples of the  $T_g$  of homopolymers and the inherent  $T_g$  thereof which permits such calculations are as follows:

	Homopolymer of	$T_g$
	<i>n</i> -octyl acrylate	$-80^\circ\text{C}$
	<i>n</i> -decyl methacrylate	$-60^\circ\text{C}$
25	2-ethylhexyl acrylate	$-70^\circ\text{C}$
	octyl methacrylate	$-20^\circ\text{C}$
	<i>n</i> -tetradecyl methacrylate	$-9^\circ\text{C}$
	methyl acrylate	$9^\circ\text{C}$
	<i>n</i> -tetradecyl acrylate	$20^\circ\text{C}$
30	methyl methacrylate	$105^\circ\text{C}$
	acrylic acid	$106^\circ\text{C}$

These or other monomers should be blended to give the desired  $T_g$  of the copolymer. As is known, for a given number of carbon atoms in the alcohol moiety, the extent and type of branching markedly influences the  $T_g$ , the straight chain products giving the lower  $T_g$ . Most of the esters of acrylic acid or methacrylic acid having a low  $T_g$  are well known in the art.

Any of the standard or other useful techniques for applying foam may be employed in this invention.

The latex which is to form the foam is preferably initially foamed to a wet foam density of .5 to .05 grams per cubic centimeter, and is then applied to the substrate in a thickness of from 10 to 300 mils. The density, of course, will vary with the presence or absence of pigments and fillers and their identity. The foam may then be dried without causing thermosetting, crosslinking or vulcanization for example by heating the foam-coated fabric at a temperature below that which causes thermosetting, crosslinking or vulcanization, for example for from 1 to 10 minutes at a temperature of from  $200^\circ$  to  $350^\circ\text{F}$ , followed, preferably after having placed the desired number of foam coated substrates together, by crushing the multiple foam coated layers to a thickness of between 5 percent and 25 percent of the original dry thickness. This will give an approximate crushed foam

density of from 0.2 to 3 g./cc.<sup>3</sup>, and is then followed by curing of the crushed foam. In general, the thickness of the dried foam prior to crushing may be substantially less than that of the wet foam, there at times being some shrinkage. This shrinkage may result in up to 30 percent of the thickness of the wet foam being lost during drying. When we talk about dry or substantially dry we mean that the moisture content of the foam will be from 5 percent to 20 percent. It is sufficient that the foam be stable enough to be self-bonded to the top film. Of course, the foam may be crushed before it is self-bonded to the surface film, but in this case it is desirable to use a crushing roll having a release coating such as a silicone or "Teflon" (Registered Trade Mark). Normally, no adhesive is needed between the foam-covered layers since a thermosettable foam is usually used and the final curing of the foam will then cause a firm bond between the layers.

It is important, we believe, to form a less dense foam then crush it since, if the initial foam is formed to the ultimate desired density by control of the amount of foaming agent or by means such as using a chemical blowing agent and restraining the expansion in order to get the final density, the walls or struts connecting the air spaces are relatively thick. A crushed foam, on the other hand, initially having expanded to a number of times its final thickness, has connecting walls or struts of a thin flexible nature. We have observed that as a result the crushed foam is much more flexible than a foam initially expanded only to the ultimate density. These foams are inherently opaque.

When pigmented compositions are contemplated, examples of the pigments that may be employed include clays, especially of the kaolin type, calcium carbonate, blanc fixe, talc, titanium dioxide, colored lakes and toners, ochre, carbon black, graphite, aluminum powder or flakes, chrome yellow, molybdate orange, toluidine red, and copper phthalocyanines. If dyed compositions are required, examples of dyes for acrylic film and foam include basic and dispersed dyes. Other composites could be made dyeable, if they are not already inherently so, through the use of additives such as methyl cellulose, hydroxyl ethyl cellulose, and the like. Other dyes which could be used include acid dyes, vat dyes, direct dyes and fiber reactive dyes.

The laminate is formed by a multiplicity of layers of pieces of the foam coated fabric, for example, from 2 to 7 layers of the foam coated fabric being placed one upon the other. The fabrics are placed in a deliberately chosen orientation of the fill and weft of each layer to those in the other layers for the achievement of desired stretch properties as hereinbefore discussed. That is not to say

that random placement is excluded; one may deliberately choose such a random arrangement and we mean to include this option as indeed a uniform arrangement is also included.

It should be noted that it is not necessary to employ additional adhesives in the lamination step. The foam coated fabrics may be laminated to one another by applying pressures up to 300 psi. Preferred ranges are 10 to 300 psi, preferably 50 to 150 psi. Temperatures may be from 150 to 300°C, and most preferably 200 to 250°C.

The final step is the application of some form of finish film, preferably clear, either as a preformed film (which may be a transfer film) or from a finish coating composition.

Suitable clear films include those cast from a single acrylic latex (thickened if necessary) or other suitable latex such as carboxylated SBR (styrene - butadiene rubber) containing antioxidants or UV stabilizers, polyvinyl chloride, poly(ethylene), poly(vinylidene chloride), poly(vinyl acetate), poly(vinyl alcohol) as well as copolymers of the monomers of these polymers. Such films may have delayed cure properties built into them where stringent durability requirements (resistance to multiple washing and drycleaning) exist.

On the other hand the film may be cast from two or more latices to achieve specific effects. For example, the "first-down" basecoat latex can be selected for its toughness and its freedom from residual tackiness. The "second-down" topcoat can be a softer material providing more plastic flow under heat and pressure to achieve embossing, lamination and heat sealing where necessary.

A finish on release paper (or other suitable release medium) can be picked up by the transfer film when it is pulled off of the release medium to provide a surface finish for other specific effects. For example, silicone surfaced release paper can be engineered so that some of the silicone goes with the film when it is pulled off the release paper to provide the water repellency.

Solvent systems can be used instead of latices alone or in combination with aqueous systems where multi-layer films are made as previously described. For example, a solvent "Saran" (Registered Trade Mark) "first-down" coat can be topped with an aqueous coating so that the composite film, when pulled off release paper and inverted, would expose a tack-free "Saran" outer surface.

The films can be made breathable by mechanically foaming the latex before casting, mechanically puncturing the film, using chemical blowing agents or dissolving or digesting out temporary fillers placed in the latex before it is cast. An example of the latter method would be the use of starch granules in the mix before casting, subsequently digesting the starch granules with an enzyme leaving pores in the film.

For special effects, the film can be colored by pigmenting the liquid medium before casting, adding dyes to the liquid medium before casting, post-dyeing the composite or vacuum metalizing the film after casting or printing the dried film. Another effect can be achieved by printing or coating the release medium with pigments or ink which would be transferred to the film after it is dried and pulled away from the release medium.

A delayed cure acrylic film is preferred as this may provide freedom from plasticizer as a means of minimizing pollution as well as avoiding the possibility that plasticizer migration will cause the foam and film to separate eventually. In addition, there is a distinct likelihood that the presence of plasticizers in either the film or the foam will cause printing inks to bleed, distorting decorative effects.

While the preferred clear (substantially transparent) film is that obtained from a cross-linkable acrylic latex as suggested herein, other crosslinkable latices are useful either as finish coating compositions or as preformed films. Examples of other latices are crude rubber in which 3 percent of the polymer is in the form of combined maleic anhydride, butadiene-styrene polymers and butadiene-acrylonitrile polymers containing 3 percent to 5 percent carboxylated groups, carboxylated polyisoprene, and other natural and artificial polymers modified to have crosslinkable or thermosettable functionality. In each case, external crosslinkers such as epoxy resins are used. As is implied by the above, the same general types of crosslinkable polymers are useful for both the clear film and the foam.

Thermoplastic preformed films which may be used include films of homopolymers and copolymers of the following monomers: vinyl chloride, ethylene, vinylidene chloride, vinyl acetate, vinyl alcohol or is poly(vinyl fluoride) poly(vinylidene chloride/vinyl chloride) polyurethane or polyester film. Similar useful preformed films can be made from ethylene-vinyl acetate, ethylene - methyl acrylate and ethylene ethyl acrylate copolymers, ionomers, vinyl chloride - propylene, vinyl chloride-ethylene and vinyl chloride - acrylate copolymers, polyethylene, nylons and chlorotrifluoroethylene, polyester and polycarbonate and thermosetting acrylic latexes. While many of the clear thermoplastic films are useful, they are not usually so desirable as the thermosetting clear film deposited from latices or, less desirably, from organic solvent solution.

If an embossed textured surface is not desired, the composite can be made by laminating with a flat pressing surface. A three dimensional effect can be achieved by using embossed rolls or plates, pressing the composite between rolls or plates at the same time as embossed paper is passed through the nip or alternatively by casting the film on

embossed release paper to such a depth that one flat film surface is achieved for printing if necessary. After bonding, the embossed release paper can be pulled away from the composite and reused. After crushing the foam and embossing, if used, the laminate is cured (thermoset, crosslinked) at a suitable temperature, for example, by heating for, for example, from 1 to 5 minutes at a preferred temperature in the range of from 135° to 190°F.

An important advantage in using a dried but uncured foam of a crosslinkable polymer and a dried but uncured clear film, printed or otherwise, is that the two elements can be passed through the nip of a pair of rollers, the distance between which is small enough to bond the two but insufficient to crush the dried foam, all without using an adhesive to bond the foam to the fabric or other substrate and to bond the foam to the clear printed or unprinted film. Of course, bonding of the dry foam and the clear film can be done at a pressure sufficient to crush the foam with or without embossing. Even after crushing, the foam has sufficient resilience to be embossed with a patterned roller. If desired, the embossing roller may be heated to the curing temperature of the thermosetting film and foam, although normally a period of time is required which necessitates passing the laminate through an oven.

For a description of suitable conventional foaming procedures and foam stabilizers and foaming agents, reference may be made to Madge, E. W., "Latex Foam Rubber", John Wiley and Sons, New York (1962) and Rogers, T. H. "Plastic Foams", Paper, Reg. Tech. Conf., Palisades Sect., Soc. Plastics Engrs., New York, November 1964. Most commonly used stabilizers and foaming agents are the alkali metal, ammonia, and amine soaps of saturated or unsaturated acids having, for example, from 12 to 22 carbon atoms. Examples of suitable soaps include tallow soaps and coconut oil soaps, preferably the volatile amine or ammonia soaps, so that the volatile portion is vaporized from the foam. Other useful foaming/foam-stabilizing agents include lauryl sulfate-lauryl alcohol, lauryl sulfate-lauric acid, sodium lauryl sulfate.

There may also be employed, as finish coat compositions, those which are extensible and flexible and contain one or more of the following ingredients: nitrocellulose, polyurethane, polyvinyl chloride, acrylic, cellulose acetate butyrate or a composition containing nitrocellulose and an isocyanate terminated prepolymer of an organic polyisocyanate with a polyester and/or polyether polyol with or without plasticizers. The preferred finish coats are the coating compositions which contain acrylic polymer or nitrocellulose and an isocyanate terminated prepolymer of an organic polyisocyanate with a polyester and/or poly-

ether polyol or contain cellulose acetate butyrate. These preferred coating compositions can provide finish coats which have better flexibility and better wear properties than those previously obtainable by using other finishes. The cellulose acetate butyrates are described in U.S. Pat. No. 3,574,154.

The amount of nitrocellulose present in one of the preferred coating compositions is from 15% to 55% based on the total solids of the composition.

These preferred coating compositions are further described in U.S. Pat. No. 3,763,061. The finish coat should preferably be applied so that there is approximately 1.0 gm. of solid topcoat per square foot of substrate in order to yield a good balance of flexibility and abrasion resistance. The finish coat addition can be controlled by the solids of the formulation, machine settings, conveyor speeds and the number of coats applied. The topcoat should be formulated at a urethane/nitrocellulose ratio of 55/45 by weight to give the best balance of properties in terms of flex, abrasion resistance and tack. This urethane/nitrocellulose ratio can be varied if necessary from 50/50 to 65/35 by weight to obtain a particular result on a specific leather but if changes are made, flex, abrasion resistance and tack should be followed. Generally, the latex coatings employed should contain latex polymer, clay, titanium dioxide or other inert fillers and foam stabilizer and may contain additive for crosslinking the polymer.

The finish compositions can be clear or can contain dulling agents, pigments, or dyes depending upon the particular use or aesthetic qualities which are desired. Examples of pigments which can be used include clay, titanium dioxide, calcium carbonate, blanc fixe, finely divided metals such as aluminum, color lakes and oxide pigments. Other conventional additives which can be used include fillers, slip agents and lubricants. The finish coat compositions preferably also contain silicone rubber polymer, such as those sold by Dow Corning and identified as DC-160, FC-227, Syl-Off-291 together with a metal organic salt catalyst, for example, dibutyl tin laurate, zinc octoate and the like. These two chemicals further improve abrasion resistance and tactile aesthetics.

The finish coat compositions can be applied to the crushed foam coated substrates by any of the techniques well-known in the art, including brushing, swabbing, spraying, curtain coating (flow coating) or dip coating. Among the useful techniques are those described in U.S. Pat. Nos. 2,126,321 and 2,884,340. One or more coats can be applied as desired. The thickness of the coating can be varied depending on the particular purposes that the coating is to serve. The amount of the finish coat applied varies according to the type of material being coated and the ultimate finish

desired. Generally, the finish coat may usefully be applied so as to provide a deposit of from 0.1 to 8 mils dry film thickness and, preferably from 0.3 to 0.5 mils dry film thickness. After application, the coating can be cured by drying to a tack-free state at room temperature for about 30 minutes to one hour, or by heating at a temperature of up to about 100°C until the desired degree of cure is effected.

An advantage of the nitrocellulose/urethane finish coat is that it forms a coating which has outstanding elastic recovery and flexibility and yet is tough enough to be used as a wear layer when applied to the laminates. These characteristics of flexibility and elastic recovery make the nitrocellulose/urethane finish coat compositions extremely valuable in the coating of thick flexible substrates subjected to severe bending action.

The following formulations are illustrative of typical formulations which may be employed for the foam (Primal is a Registered Trade Mark):

Formulation 1		Parts by Weight
83BA/14AN/1Ac/TAA		
Copolymer	100	
China Clay	15	
Ammonium Stearate (33%)	7.0	
Diethylenetriamine	0.6	
Ammonium Hydroxide	2.0	
Primal Non-Bleeding Red Colorant	15.0	
Formulation 2		Parts by Weight
82.5BA/14AN/1.5Ac/2AA		
Copolymer	500.0	
Clay	75.0	
Ammonium Stearate	35.0	
Diethylenetriamine	3.5	
Ammonia (28%)	10.0	
Primal Brown Colorant	75.0	
Water	65.0	
Formulation 3		Parts by Weight
86EA/10AN/4MOA		
Copolymer	565.5	
Clay	75.0	
Ammonium Stearate	35.0	
Aqueous melamine formaldehyde resin	11.5	
Ammonia (28%)	10.0	
Primal White 264 Colorant	75.0	

## Formulation 4

Parts by Weight	
65.5	H <sub>2</sub> O
10.0	NH <sub>3</sub> (28%)
75.0	Clay
75.0	Primal Black 110
65	96EA/3.5AM/0.5AA
500.0	Copolymer
35.0	Ammonium Stearate

## Formulation 5

Parts by Weight	
75.0	Primal Black 110
10.0	NH <sub>3</sub> (28%)
75.0	Clay
65	96EA/3.5AM/0.5AA
565.5	Copolymer
35.0	Ammonium Stearate
75	Aqueous melamine formaldehyde resin
11.5	

## Formulation 6

Parts by Weight	
75.0	Primal Ochre Yellow
10.0	NH <sub>3</sub> (28%)
75.0	Clay
80	96EA/3.5AM/0.5AA
565.0	Copolymer
35.0	Ammonium Stearate
11.5	Melamine resin

The components of Formulations 1 to 6 may be added to the mix in the order given (except for the NH<sub>3</sub> which is split into two feeds; half being saved until after the melamine resin, Aerotex MW, has been added) and stirred thoroughly—"Lightnin" (Registered Trade Mark) mixer, Talboys mixer or "Cowles Dissolver" (Registered Trade Mark)). Any other melamine resin may be employed such as those sold as Aerotex M-3, melamine-formaldehyde-methanol, methoxylated melamine formaldehyde. After mixing, the formulated mix is covered to prevent skinning over.

## Formulation 7

Parts by Weight	
100	83BA/14AN/1Ac/2AA
420.5	Copolymer
25.8	Ammonium Stearate
21.5	Octylphenoxy polyethoxy ethanol
105	"Acme" (Registered Trade Mark) WW Clay
57.5	Primal Black 110
41.7	NH <sub>3</sub> (25%)
7.0	Polyethylene Wax
23.9	Diethylene triamine
2.1	
600.0	
110	



In this formulation latex and non-ionic surfactants are added to a Cowles dissolver and stirred slowly. To this is added the ammonium stearate. The agitation is increased while slowly adding the remaining ingredients in the order given. After a uniform suspension is obtained, the formulation is filtered through a cheese cloth or mesh screen (40 mesh). This material is then ready to be employed with an appropriate blowing agent. By substituting for the colorant, Primal Black 110, other suitable colorants, other formulations can be prepared in substantially the same manner.

Some preferred examples of the invention will now be described, for the purposes of illustration only.

#### EXAMPLE 1

Doubled Crushed Foam Crepe Fabric Having a Top Layer of an Acrylic Film

An emulsion copolymer dispersion prepared from 48.25 parts of butyl acrylate, 48.25 ethyl acrylate, 3 parts N - methylol acrylamide and 0.5 parts itaconic acid (100 g.) is formulated with titanium dioxide (50%, 25 g.), a melamine formaldehyde resin (2.3 g., Aerotex MW), ammonium stearate (7.0 g.), "Acrysol" (Registered Trade Mark) ASE-60 (3.0 gm) acid-containing crosslinked acrylic emulsion copolymer thickener premixed with water (3.0 g.) and ammonium hydroxide (2.0 g., 28%). The ingredients are mixed and foamed in a kitchen aid mixer (Model C) to a wet density of about 0.2 g./cc. The foam is then applied to a polyester crepe at a thickness of 100 mm (wet) and then dried for 3 minutes at 138°C. The dried foam coated crepe is then covered by another dry foam coated crepe and then coated with a film prepared as follows: On a silicone coated release paper 5 mils thick a latex (50% solid) of 72 parts butyl acrylate, 20 parts acrylonitrile, 3.5 parts methacrylamide, 3.5 parts N - methylol acrylamide and 1 part itaconic acid is cast in a thickness to afford a dry film 2 mils thick. This coated paper is then dried at 95°C for 3 minutes. The release paper is removed to afford the desired film. The entire double crushed foam coated crepe laminate coated with the film is subjected to pressure of about 100 psi for 3 seconds at 121°C. The composite is then given a final cure at 150°C for 5 minutes. The product obtained is 41 mils thick, has soft, resilient leather like hand.

#### EXAMPLE 2

Double Crushed Foam Polyester (60)/Cotton (40)

By following substantially the procedure as described in Example 1, and by substituting for the crepe employed therein a substrate prepared from polyester (60) and cotton (40),

there is obtained a composite 25 mils thick which is moderately resilient.

#### EXAMPLE 3

A composite of Film/Crushed Foam/Crepe/Crushed Foam/80<sup>2</sup> Cotton

By following substantially the procedure described in Example 1 by substituting for one of the crushed foam coated crepe layers a crushed foam coated 80<sup>2</sup> cotton layer there is obtained a composite of film/crushed foam/crepe/crushed foam/80<sup>2</sup> cotton of 32 mils thick which is moderately resilient.

#### EXAMPLE 4

A composite of a Film/Crushed Foam/Rayon challis Crushed Foam/Rayon challis

By following substantially the procedure described in Example 1 by substituting for the polyester crepe recited therein rayon challis there is obtained a composite of a film/crushed foam/rayon challis/crushed foam/rayon challis 38 mils thick.

#### EXAMPLE 5

Film/Crushed Foam/Crepe/Crushed Foam/Crepe

An emulsion copolymer dispersion prepared from 65 parts ethyl acrylate, 25.5 parts butyl acrylate, 4.5 parts acrylonitrile, 3.5 parts acrylamide and 1.5 parts itaconic acid (T<sub>300</sub> equals -12°C) is formulated with Primal Ochre (15 g.), water (10 g.), a melamine-formaldehyde resin (2.3 g.), Aerotex MW, ammonium stearate (7.0 g., 33%) and ammonium hydroxide (2.0 g.). The mixture is foamed to about 0.2 g./cc and applied (100 ml., wet) to brown crepe and dried for 3 minutes at 120°C. After assembling two such coated crepe layers, the top foam is covered with an acrylic film prepared in a manner described in Example 1 having the following composition: 62% butyl acrylate, 30% methyl methacrylate, 3.5% N - methylol acrylamide, 3.5% methacrylamide and 1% itaconic acid. The composite is crushed and cured as described in Example 1. The crushing employed an embossing plate to afford a leather-like grain appearance.

#### EXAMPLE 6

Bias orientation of Fabric

By following substantially the procedure described in Example 1, except that instead of placing the fabrics oriented with the warp direction parallel, the foam coated fabrics are orientated at a 45° angle and by substituting for the film described in Example 1 the film described in Example 5, there is obtained a composite with a stretch which is more isodirectional than the composite of Example 1.

**EXAMPLE 7**

Film/Crushed Foam/Acetate Tricot/Crushed Foam/Acetate Tricot

By following substantially the procedure of Example 1 and by employing in place of the polyester crepe fabric employed therein, acetate tricot and by laminating the foam coated fabrics, there is obtained a double crushed foam acetate tricot fabric having a top layer of an acrylic film. The resilience of the composite is less than that of the product of Example 1 but has better drape than the product of Example 1.

**EXAMPLE 8**

Crushed Foam/Crepe/Crushed Foam/Crepe/Urethane Topcoat

A formulation is prepared from the same emulsion copolymer employed in Example 5 (100 g.) along with Primal Dark Brown (15 g.), Prime Ochre (6 g.), red pigment paste (3 g.), water (10 g.), ammonium stearate (7 g.) and ammonium hydroxide (2 g.). Foam coated crepe layers are prepared and assembled as in Example 5. These layers are then crushed employing an embossed plate to afford a composite having a pattern. The upper crushed foam layer is sprayed with a urethane solution, dried and the total composite is cured at 150°C for 5 minutes.

**EXAMPLE 9**

Film/Crushed Foam/Crepe/Crushed Foam/Crepe

By following substantially the procedure in Example 7, employing crepe instead of tricot and, as the emulsion copolymer for the foam, the emulsion described in Example 1, there is obtained a film/crushed foam/crepe/crushed foam/crepe composite with a resilient hand.

**EXAMPLE 10**

Crushed Foam/Crepe/Crushed Foam/Cotton Twill/Urethane Coating

By following substantially the procedure described in Example 9 and by substituting for one of the crepe substrates a crushed foam coated cotton twill, there is afforded a crushed foam/crepe/crushed foam/cotton twill/urethane coating composite.

**EXAMPLE 11**

Three Layer Fabric/Foam Composite

Foam, as prepared in Example 1, is applied to polyester crepe, 100 mil wet foam, and dried 3 minutes at 138°C. Three sections of this crepe/foam are stacked on top of each other, foam side up. A film of dried latex of composition 72 parts butyl acrylate, 20 parts acrylonitrile, 3.5 parts methacrylamide, 3.5 parts N-methylol acrylamide and 1 part itaconic acid, prepared as described in Example 1, is placed on top of the triple

foam/crepe stack. The entire stack is crushed at 100 psi with an embossed plate heated to 115°C for 5 seconds. The crushed composite is cured 5 minutes at 150°C. This final cured composite has a resilient, moderately firm, leather-like hand.

By employing substantially the procedure described in Example 11 and by employing 5, 6 or 7 layers of foam/crepe, there are prepared 5, 6 and 7 layer fabric/foam composites. These composites can be finished with a topcoat or a film as described in the following examples:

**EXAMPLE 12**

Four Layer Fabric/Foam Composite

This composite is prepared substantially by the procedure of Example 11, employing four layers of the foam/crepe which are stacked on top of one another and covered with the film before crushing is accomplished.

**EXAMPLE 13**

Finish Coat and Application

Step A—Preparation of Prepolymer

To a two liter, three-necked flask fitted with a mechanical stirrer, thermometer, distillation head, condenser, nitrogen bleed valve and vacuum source is charged 500.5 g. of a polyether triol (MW=1540). The pressure is reduced to 51 mm. of Hg and the temperature raised to 70°C while agitating the mixture. The distillate, 45.5 g., is collected and the temperature reduced to 30°C while the pressure is brought to 760 mm. of Hg with a nitrogen bleed. Three hundred and five grams toluene diisocyanate are added to the reaction mixture and the temperature is raised to 75°C for 16 hours. The isocyanate content is determined and the product cooled to room temperature. The prepolymer has the following properties: % solids—74.21; Meq. NCO/g. solution—0.834; G.H., Viscosity—T+; Residual TDI—1.17.

Step B—Preparation of Finish Coat Composition

The finish coat composition is prepared by mixing the following ingredients (parts by weight): prepolymer of Step A (110), nitrocellulose (177), nitrocellulose plus a dulling agent (100), black pigment, plasticizer and nitrocellulose (200), butyl acetate, xylene and 2-ethoxyethyl acetate (413 parts in a ratio of 50:40:10), a silicone rubber polymer (25, "Dow Corning—160") and dibutyl tin laurate (50).

Step C—Application

The composition of Step B is applied to the leather or leather-substitute using standard spray equipment such that about 1.0 g. of solids per square foot of substrate is obtained.

## EXAMPLE 14

## Finish Coat and Application of Cellulose Acetate Butyrates

## Step A

5 Poly(1,3 - butylene adipate) (97.5 parts) is obtained by a conventional process, having a molecular weight of 5000 and a hydroxy number of 20, is thoroughly dehydrated by sparging with nitrogen at 130°—140°C. The polyester is then cooled to 106°—108°C and 4.6 parts of methylene - bis(4 - phenylisocyanate) is added over a period of 15 minutes. The temperature of the reaction mixture is raised to 110°—115°C and mixing is continued under a positive pressure of nitrogen for 30 hours. The cooled product has a viscosity of about one million poises and is a light-colored stiff gum. A 50% solution in xylene has a Gardner Holdt viscosity of Z-6.

## 20 Step B—Formulation of Clear Plasticized Cellulose Acetate Butyrate Solution

A solvent mixture is prepared by blending 510 parts of toluene, 170 parts of methyl ethyl ketone and 320 parts ethyl alcohol. To 69 parts of this solvent mixture are added 15.1 parts of 3 second viscosity cellulose acetate butyrate comprising 20% butyryl and 25% acetyl content followed by 3.8 parts of a linear polyester, namely, poly(propylene glycol sebacate) having a molecular weight of 8000 and 12.1 parts of a 50% solution in xylene of the extended polyester of Example A. The mixture is agitated until a homogeneous solution is obtained. The mixture is pale straw colored and has a viscosity of 2100 centipoises.

## Step C—Application

20 Twenty parts of the clear finish of Step B is mixed with 80 parts of methyl ethyl ketone and 1 part of a red spirit-soluble dye is added. The mixture is applied by spray-coating to a piece of crushed foam coated leather substitute at the rate of 1.0 g. solids per square foot of leather substitute. The finish is air dried and then embossed at 20 psi and 160°F for 60 seconds with a sand-blasted platen. The resulting finish has a warm brown color and possesses outstanding resistance to cracking or dulling when flexed.

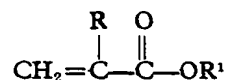
## 50 WHAT WE CLAIM IS:—

1. A laminate of two or more layers of crushed foam (as hereinbefore defined) coated fabric (as hereinbefore defined), the laminate having a surface finish film.
2. A laminate as claimed in Claim 1 comprising from 2 to 7 layers of crushed foam coated fabric.
3. A laminate as claimed in Claim 1 or 2 wherein the fabric comprises cotton twill, broadcloth, acetate crepe, polyester crepe, polyester knit, double knit, nylon taffeta, nylon tricot, fiberglass, woollen fabric, worsted,

flocked fabric rayon fabric, or a blend of natural and synthetic fibers or imitation leather.

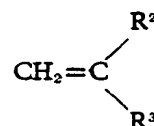
4. A laminate as claimed in any preceding Claim wherein the foam comprises a polymer of a mixture of at least two of the following monomers, of which at least one is a monomer which contains functional groups capable of crosslinking:

- (a)  $\alpha,\beta$ -ethylenically unsaturated acid,
- (b) monomer of the formula



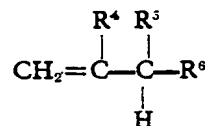
wherein R is hydrogen or alkyl and R<sup>1</sup> is a straight, branched or cyclic alkyl, alkoxy-alkyl, or alkylthioalkyl radical having from 1 to 20 carbon atoms, cyclopentyl, cyclohexyl, ureido, hydroxy (C<sub>1</sub> to C<sub>5</sub>)alkyl, 2,3-epoxy propyl, amino (C<sub>1</sub> to C<sub>5</sub>)alkyl, mono or di(C<sub>1</sub> to C<sub>5</sub>)alkyl or hydroxy(C<sub>1</sub> to C<sub>5</sub>)alkyl substituted amino(C<sub>1</sub> to C<sub>5</sub>)alkyl,

- (c) monomer of the formula



wherein R<sup>2</sup> is hydrogen or methyl; and R<sup>3</sup> is halo, alkanoyloxy, cyano, phenyl, formyl, carbamoyl, epoxy, N - hydroxy methylcarbamoyl, tolyl, methoxy methyl, 2,4 - diamino - tri - azinyl(C<sub>1</sub> to C<sub>5</sub>)alkyl or

- (d) monomer of the formula



wherein R<sup>4</sup> is hydrogen or methyl; R<sup>5</sup> and R<sup>6</sup> are (C<sub>1</sub> to C<sub>5</sub>)alkoxy or (C to C<sub>5</sub>)alkanoyloxy.

5. A laminate as claimed in any preceding Claim wherein the finish coating comprises a transparent preformed film or transparent coating of one or more of the following: melamine resin, urea - formaldehyde condensate, nitrocellulose, polyurethane, poly(vinyl chloride), acrylic resin, cellulose acetate butyrate, nitrocellulose modified polyurethane.

6. A laminate as claimed in any of Claims 2 to 4 wherein the finish film is a preformed film comprising a polymer of one or more of the following monomers: vinyl chloride, ethylene, vinylidene chloride, vinyl acetate, vinyl alcohol; or is poly(vinyl fluoride), poly(vinylidene chloride/vinyl chloride), polyurethane or polyester film.

7. A laminate as claimed in any of Claims

- 2 to 4 wherein the finish film is a preformed film of a thermosetting acrylic latex.
8. A laminate as claimed in Claim 6 or 7 wherein the finish film has a printed design thereon.
9. A laminate as claimed in any of Claims 2 to 6 wherein the finish film is formed from a coating composition applied thereto and containing acrylic polymer, nitrocellulose and an isocyanate terminated prepolymer of an organic polyisocyanate with a polyester and/or polyether polyol.
10. A laminate as claimed in Claim 9 wherein the finish coating contains from 15—55% by weight nitrocellulose.
11. A laminate as claimed in any preceding Claim wherein the finish coating is from 0.1 to 8 mils thick.
12. A laminate as claimed in Claim 1 substantially as described in any one of the foregoing Examples.
13. A simulated leather comprising a laminate as claimed in any preceding Claim.
14. A process for the production of a laminate which comprises forming, on textile material, a layer of foam of polymer latex, drying the thus coated material to stabilise the foam, laying two or more pieces of foam covered textile one upon the other(s), subjecting the superimposed layers to heat and pressure to crush and cure the foam and applying a finish coating to the laminar material before or after crushing and curing.
15. A process as claimed in Claim 14 in which the superimposed layers are subjected to a pressure of from 10 to 300 p.s.i. at a temperature of from 150 to 300°C.
16. A process as claimed in Claim 14 or 15 in which the foam on the foam coated textile is dried to a moisture content of 5 to 20 percent by weight.
17. A process as claimed in any of Claims 14 to 16 in which the drying step is carried out at a temperature of from 200 to 350°C.
18. A process as claimed in any one of Claims 14 to 17 as applied to the production of a material as claimed in any one of Claims 2 to 13.
- For the Applicants:  
P. W. S. WOOD,  
Chartered Patent Agent,  
Rohm and Haas Company,  
European Operations,  
Chesterfield House,  
Barter Street,  
London, WC1A 2TP.